



## SYNTHESIS, PHYSICO-CHEMICAL CHARACTERIZATION AND BIOCIDAL STUDIES OF NICKEL (II) MIXED-LIGAND COMPLEXES OF ALKYL DITHIOCARBAMATE AND SALICYLALDEHYDE

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### ABSTRACT:

Six mixed ligand complexes of Nickel (II) ion containing salicylaldehyde and alkyl dithiocarbamate bases were prepared. The complexes were characterized with electronic and infrared spectroscopy, conductance measurement, melting point and percentage metal analysis. Resulting analytical data indicates that the salicylaldehyde and dithiocarbamate groups are coordinated to the nickel ion in a bidentate fashion. A tentative square planar geometry was assigned to all the complexes. The complexes were proposed to have a general formulae of  $[\text{Ni}(\text{Sal})(\text{Rdtc})]$ , where Sal = salicylaldehyde; R = diethylamine ( $\text{Et}_2\text{NH}$ ), n-dibutylamine ( $\text{n-Bu}_2\text{NH}$ ), iso-dibutylamine ( $\text{i-Bu}_2\text{NH}$ ), cyclohexeneamine ( $\text{c-HxNH}$ ), methylbutylamine ( $\text{MeBuNH}$ ), ethylbutylamine ( $\text{EtBuNH}$ ) and dtc = dithiocarbamate anions. The metal complexes were screened against gram positive bacteria (*Bacillus cereus* and *Staphylococcus aureus*) and gram negative bacteria (*Klebsiella Oxytoea*, *Pseudomonas aureginosa* and *Escherichia coli*) using Agar diffusion test. The complexes recorded a low to moderate activity against the screened pathogens.

### KEYWORDS:

Alkyl dithiocarbamate, Salicylaldehyde, Nickel ion, Antibacterial activities.

### INTRODUCTION

Metal complexes play an essential role in agriculture, pharmacy, medicine and chemical industries (Shalin et al. 2009). Complexes of Salicylaldehyde were among the first chelate systems to have been studied by infrared spectroscopy (Percy and Thornton, 1973). Since then extensive physicochemical characterizations have been applied to the study of salicylaldehyde complexes using different analytical techniques. Metal complexes of Salicylaldehyde have shown diverse applications in medicine, catalysis, analytical chemistry, material science e.t.c.

Similarly, dithiocarbamate metal complexes are known for their various applications (Leka et al. 2006), which include vulcanization accelerators, high-pressure lubricants, and active ingredients of fungicides, pesticides and pharmaceutical products (Takagi and Tanaki, 1949, Manohar et al. 2006, and Balasubramaniam et al. 2007). This kind of compounds has been reported in literature to show detoxicant and immunopharmacological properties, such as antibacterial, antifungal etc (Amna. 2001). Also, they have been reported as group of useful bridging ligands for creating mixed valence polynuclear systems (Ryo et al. 2006).

An extensive search through literature showed that many mixed ligand dithiocarbamate complexes with Schiff base moiety as part of its coordinating ligand have been widely reported (Amna. 2001, and Gruber et al. 1968). However, mixed ligand dithiocarbamate complexes without a Schiff base moiety are seldom reported in literature, Therefore, six novel Ni(II) mixed ligand complexes containing different alkyl dithiocarbamate anions and a salicylaldehyde moiety were prepared and characterized. The resulting complexes were screened for their antibacterial activity.

### MATERIALS AND METHODS

#### Reagents and solvents

All reagents and solvents used for this work were of analytical reagent grade (bought from Aldrich and Sigma Co. and British Drug House) and used as supplied.

#### Physical measurements

The experimental percentage nickel content of the complexes was determined by chelatometric titration using murexide as an indicator. Electronic spectra were obtained using Genesys 10 UV Spectrophotometer. Infrared spectra were obtained using Buck 500 model spectrophotometer. Electrolytic conductivities of  $1 \times 10^{-3}$  M solution of the complexes in DMF were determined using Hanna conductivity meter model H19991300.

## SYNTHESIS

Preparation of sodium *N*-methyl-*N*-butyl dithiocarbamate

The reaction involved stirring carbon disulfide with a secondary methylbutylamine in the presence of

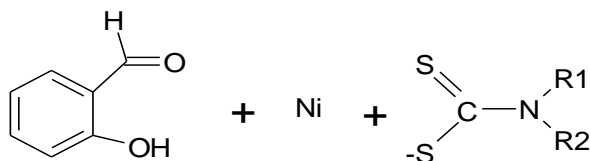
concentrated aqueous NaOH at about 0 °C leading to the formation of sodium *N*-methyl-*N*-butyl dithiocarbamate. This method was used to synthesize all the alkyl dithiocarbamates.

### Equation of reaction

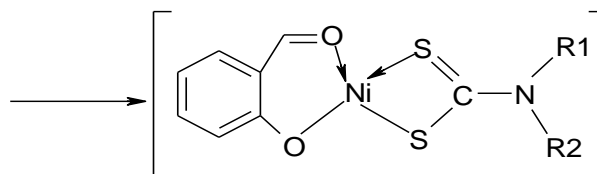


General method for the preparation of mixed ligand complexes

1:1 mole ratio of aqueous methanol solution of sodium *N*-methyl-*N*-butyl dithiocarbamate and salicylaldehyde was mixed and stirred continuously. Nickel salt was added to the stirring methanol solution. The mixture was refluxed for 3hrs.



Precipitates formed were cooled, filtrated under suction and washed with methanol and diethylether. The product was dried over night under silica gel in the desiccator. This procedure was used for the preparation of all the nickel(II) mixed ligand complexes. See **Figure 1.0**.



**Mixed ligand complex**

Where R<sub>1</sub>R<sub>2</sub> = various alkyl groups

**Fig 1.0: Proposed structure of the reaction mechanism for all the mixed ligand complexes**

### Antibacterial screening

The in vitro evaluation of antibacterial activity was performed using the agar diffusion technique. Three gram negative bacteria (*Klebsiella oxytoea*, *Pseudomonas aureginosa*, *Escherichia coli*) and two gram positive bacteria (*bacillus cereus* and *staphylococcus aureus*) were resuscitated from a nutrient slope and grown in nutrient broth at 37°C for 24 hours. The surface of a petri dish was uniformly inoculated with 0.2 ml of 24-hour old test bacteria culture. Using a sterile cork borer, 7 mm wells were bored into the agar. Then 10 mg/ml solution of each test compounds in DMF was added to the well bored. The plates were kept after inoculation at 37°C for 24hours, after which the inhibitory zone (in mm) were taken as a measure of antibacterial activity.

## RESULTS AND DISCUSSION

Colour, percentage yield, conductance measurement, melting point and percentage nickel content:

The complexes showed different shades of green colour ranging from light green, dark green to lemon green. The complexes showed from moderate to high percentage yield. Experimental percentage nickel in the complexes agrees well with the theoretical values, suggestive of a four coordinate geometry for the complexes. The melting points of the mixed complexes were recorded in degree Celsius and showed distinct variations, supportive of the formation of different complexes. The molar conductance of all the complexes in DMSO were in the range of 12-25 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating they are non electrolyte, since a value of 60-90 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> is expected for a 1:1 electrolyte (Rajavel *et al.*, 2008). The results were tabulated in **Table 1.1**.

**Table 1.1: physical and analytical data of the complexes**

S. No	Complexes Emperical Formula	F.Weight (Grams)	% Yield	%Ni	Melting Point °c	Conductance (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Colour
1	Ni(Sal)(c-HxMedtc)	368.15	66.96	15.95(16.05)	*200	12.00	Light Green
2	Ni(Sal)(Et <sub>2</sub> dtc)	328.10	92.20	17.89(17.86)	*160	25.00	Green
3	Ni(Sal)(n-Bu <sub>2</sub> dtc)	384.19	58.53	15.28(15.17)	*180	10.00	Green
4	Ni(Sal)(i-Bu <sub>2</sub> dtc)	384.19	68.70	15.28(15.12)	*196	18.00	Lemon green
5	Ni(Sal)(EtBudtc)	356.14	44.16	16.49(16.48)	*178	16.00	Green
6	Ni(Sal)(MeBudtc)	342.12	72.93	17.16(17.23)	*192	15.00	Green

\*Decomposition temperature, Ni (T) = Theoretical percentage nickel.

Table 1.2: Infrared spectra of the mixed ligand complexes

S/n	COMPLEXES	$\nu_{C=O}$	$\nu_{C-C}$	$\nu_{C-O}$	$\nu_{C-S}$	$\nu_{Ni-O}$	$\nu_{Ni-S}$
1	Ni(Sal)(Et2dtc)	1624s	1522s	1242s	992m	523m	311m
2	Ni(Sal)(n-Bu2dtc)	1626s	1535s	1245m	1027s	528w	320m
3	Ni(Sal)(i-Bu2dtc)	1651s	1530s	1253s	1034m	533vs	318s
4	Ni(Sal)(EtBudtc)	1647vs	1529s	1237s	1034w	533m	320m
5	Ni(Sal)(MeBudtc)	1647w	1530w	1261w	967w	533m	305m
6	Ni(Sal)(cHxMedtc)	1650vs	1529vs	1251m	1034s	533vs	308s

vs = very strong, s = strong, m = medium, w = weak and vw = very weak

Table 1.3: Electronic reflectance spectra of the complexes

S/N	COMPLEXES	BANDS kK	ASSIGNMENT	TENTATIVE GEOMETRY
1	Ni(Sal)(Et2dtc)	12.15 24.06 38.60 49.63	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $\pi \rightarrow \pi^*$ Charge transfer	Square planar
2	Ni(Sal)(n-Bu2dtc)	12.32 16.40 30.70 40.57	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $\pi \rightarrow \pi^*$ Charge transfer	Square planar
3	Ni(Sal)(i-Bu2dtc)	16.03 24.24 30.47 42.96	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $\pi \rightarrow \pi^*$ Charge transfer	Square planar
4	Ni(Sal)(EtBudtc)	16.40 24.16 39.60 48.06	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $\pi \rightarrow \pi^*$ Charge transfer	Square planar
5	Ni(Sal)(MeBudtc)	16.15 24.71 30.57 41.03	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ $\pi \rightarrow \pi^*$ Charge transfer	Square planar
6	Ni(Sal)(c-HxMedtc)	16.57 24.81 41.03 48.06	$^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$ Charge transfer Charge transfer	Square planar

kK = kiloKaysar (1kK = 1000cm<sup>-1</sup>)

#### Infrared Spectral Studies

The principal infrared bands of the mixed ligand complexes are presented in Table 1.2. The peak for the  $\nu_{C=O}$  stretching vibration was in the range of 1624-1651cm<sup>-1</sup> for the complexes. The absence of peaks around 3300-3500 cm<sup>-1</sup> proves the deprotonation of the salicylaldehyde phenolic hydrogen due to coordination to the nickel ion via the phenolic oxygen. The appearance of peaks around 500-590 and 300-350cm<sup>-1</sup> was attributed to the  $\nu_{Ni-O}$  and  $\nu_{Ni-S}$  stretching vibrational bands respectively. This further proves the coordination of the ligands to the nickel ion.

#### Electronic Spectra:

The principal features of the visible and ultraviolet spectra of the complexes showed bands around 30-

39kk which are due to intraligand  $\pi \rightarrow \pi^*$  transition, intense bands above 40kk region are due to either metal-ligand or ligand-metal charge transfer and weak bands at 490 and 650nm are due to d-d transitions. According to literature, transitions around 13-16kk were assigned to  $^1A_{1g} \rightarrow ^1A_{2g}$ , and 20-24kk to  $^1A_{1g} \rightarrow ^1B_{1g}$  of a square planar geometry (Amna, 2001). Bands around 30-39kk were assigned to  $\pi \rightarrow \pi^*$  transitions and above 40kk were given charge transfer assignments. The complexes had absorption bands indicative of square planar nickel (II) geometry and were assigned as such. The electronic spectra data were tabulated and shown in Table 1.3.

#### Antibacterial screening

The complexes had low to moderate activity against *Klebsiella oxytoea*, *Pseudomonas aureginosa* and

*Staphylococcus aureus*. They were not active against *E.coli* and *Bacillus cereus*.

Table 1.4: Antibacterial Screening

Test compounds	<i>Escherichia coli</i>	<i>Klebsiella oxytoea</i>	<i>Pseudomonas aureginosa</i>	<i>Staphylococcus aureus</i>	<i>Bacillus cereus</i>
Ni(Sal)(Et2dtc)	R	13.5±0.7	R	14.5±0.7	R
Ni(Sal)(n-Bu2dtc)	R	R	R	14.5±0.7	R
Ni(Sal)(i-Bu2dtc)	R	16±0.7	R	16.5±0.7	R
Ni(Sal)(EtBudtc)	R	R	R	17.5±0.7	R
Ni(Sal)(MeBudtc)	R	13.5±0.7	22.0±1.4	10.5±0.7	R
Ni(Sal)(cHxMedtc)	R	12.5±0.7	R	13.5±0.7	R
Streptomycin	24.5±6.4	29.5±0.7	25±0	21.5±0.7	21.5±0.7
DMF	R	R	R	R	R

R = Resistant, +Streptomycin = Positive standard and Dimethylformamide = Negative standard

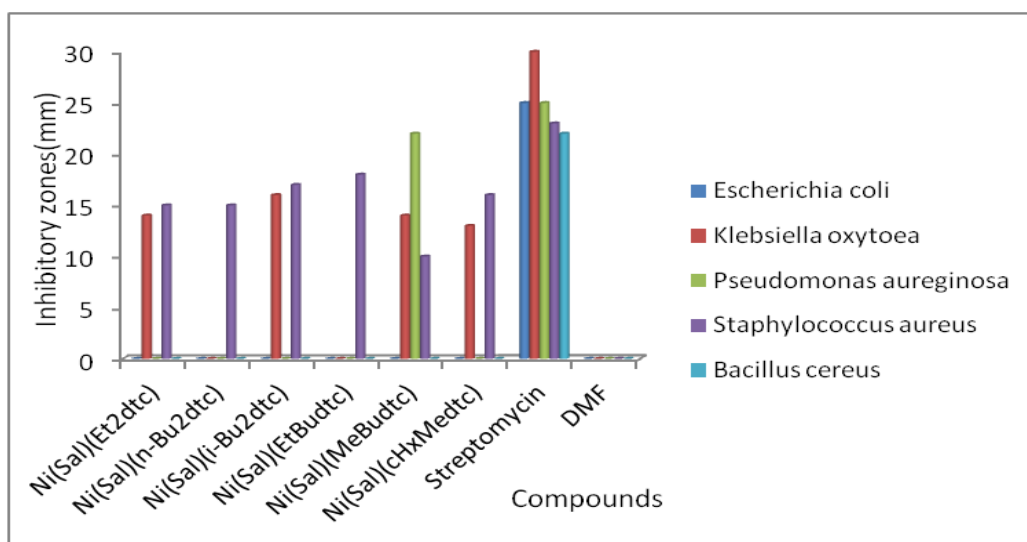


Fig 1.1: Histogram representation of the antibacterial screening of the mixed ligand complexes.

## CONCLUSION

The six alkyldithiocarbamate and salicylaldehyde ligands were coordinated to the metal ions via the carbonyl and phenolic oxygen of the salicylaldehyde compound, and thio group of the dithiocarbamate compound. The  $\nu_{C-S}$  stretching vibrational band of the dithiocarbamate moiety in the mixed ligand complexes showed a single sharp band around  $977\text{cm}^{-1}$  which credits to a bidentate coordination pattern of the two sulfur donors of dithiocarbamate ligand to the nickel ion according to literature (Amna, 2001). Metal analysis data of the mixed ligand complexes also gave support to the presence of the novel complexes as experimental percent nickel corresponds to that of the theoretical percent nickel.

The electronic spectra measurement was corroborative of a 4- coordinate square planar geometry for the

complexes. The complexes mostly exhibit mild *in-vitro* antibacterial activities against most the bacteria used, mostly against *Staphylococcus aureus*. The [Ni (Sal) (MeBudtc)] complex had broad spectrum anti-bacteria activity against *pseudomonas aeruginosa*, proving their potentials as broad-spectrum antibacterial agent.

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**\* Ekennia\* Anthony. C and Odola Adekunle. J; SYNTHESIS, PHYSICO-CHEMICAL CHARACTERIZATION AND BIOCIDAL STUDIES OF NICKEL (II) MIXED-LIGAND COMPLEXES OF ALKYL DITHIOCARBAMATE AND SALICYLALDEHYDE**

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